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# Macromers by Carbocationic Polymerization

## 3. Reactivity Ratios in Macromer/Small Monomer Copolymerizations

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### Summary

The validity of the copolymer composition equation for the copolymerization of macromers with small monomers for the preparation of graft copolymers has been examined. The reactivity ratios of high molecular weight macromers $r_1$ cannot be determined experimentally with sufficient accuracy whereas those of small monomers $r_2$ may be calculated by $r_2 = \ln(1-p_2)/\ln(1-p_1)$, where $p_1$ and $p_2$ are the respective conversions of the macromer and small monomer. A single experimental datum obtained even at high conversions may be used. The error of the method can be readily calculated.

### Introduction

Macromolecular monomers (macromers) are extremely useful new materials, particularly as comonomers for the synthesis of heretofore unavailable well defined graft copolymers, e.g., poly(methyl methacrylate-g-isobutylene)(1,2). The synthesis of graft copolymers by the macromer technique can be readily accomplished by copolymerization of the macromer with select conventional small-molecule monomers. It is important to elucidate the monomer reactivity ratios in macromer copolymerization systems since these parameters govern the overall composition of the graft copolymer. Also, the effect of macromer molecular weight, conformational and steric effects on the mechanism of copolymerization could be studied by determining the reactivity ratios of macromers having various molecular weights.

In the course of our fundamental research on macromers we have examined in quantitative terms peculiarities associated with the experimental determination of macromer reactivity ratios. This communication concerns a simple integrated equation useful for the determination of the reactivity ratios of small monomers in macromer/small monomer copolymerizations and an illustration of the use of this equation for the preparation of poly(methylmethacrylate-g-isobutylene).

### Kinetic Scheme

The propagation and cross-propagation events in a copolymerization of a macromer $M_1$ with a small monomer $M_2$ are described by the following set of equations:

$$\sim M_1^* + M_1 \xrightarrow{k_{11}} \sim M_1^* \qquad (1)$$

$$\sim M_1^* + M_2 \xrightarrow{k_{12}} \sim M_2^* \qquad (2)$$

$$\sim M_2^* + M_1 \xrightarrow{k_{21}} \sim M_1^* \qquad (3)$$

$$\sim M_2^* + M_2 \xrightarrow{k_{22}} \sim M_2^* \qquad (4)$$

where the asterisk indicates the active propagating species (free radical, carbocation, etc.). The reactivities of the propagating species are assumed to be affected only by the electronic and steric structure of the chain end, and should be independent of the molecular weight of the active species. This kinetic model yields the well-known copolymerization composition equation (3):

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{1 \;\; + r_1([M_1]/[M_2])}{r_2 + [M_1]/[M_2]} \qquad (5)$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$

Equations (1) and (3), characterized by rate constants $k_{11}$ and $k_{21}$, respectively, refer to reactions between two large species, i.e., the addition of a macromer molecule $M_1$ to a growing chain $\sim M_1^*$ or $\sim M_2^*$. These events, similarly to bimolecular termination reactions in free radical polymerizations (4), are most likely diffusion-controlled. Thus the incorporation of macromers into the growing copolymer chain would also be diffusion-controlled and would result in a corresponding decrease in $r_1$ and increase in $r_2$.

In copolymerization charges consisting of macromers plus small monomers the mole concentration of the macromer relative to that of the small monomer is necessarily extremely low, while their relative weight concentrations are similar. The higher the molecular weight of the macromer the larger the molar disparity. If the number average molecular weight of the macromer $\overline{M}_{n1}$ is very much larger than that of the small monomer $\overline{M}_{n2}$ (i.e., $\overline{M}_{n1} >> \overline{M}_{n2}$) the following simplifications hold:

$$1 >> r_1[M_1]/[M_2] \quad \text{and} \quad r_2 >> [M_1]/[M_2]$$

and eq (5) can be reduced to

$$\frac{d[M_1]}{d[M_2]} \approx \frac{[M_1]}{[M_2]} \cdot \frac{1}{r_2} \qquad (6)$$

According to this pseudo one parameter copolymerization composition equation the copolymer composition is governed by $r_2$ i.e., by the relative rates of reactions shown by eqs (3) and (4).

## Analysis and Discussion

Monomer reactivity ratios of conventional small monomers are usually determined by linear least square methods (3,5,6,) or non-linear methods (7,8). These methods require a suitably large number of copolymer composition data obtained over a wide range of monomer concentrations (mole fractions) and in the absence of such data incorrect results may be obtained. In the copolymerization of a macromer with a small monomer it would be very difficult if not impossible to generate copolymer composition data reflecting a wide range of charge compositions because of the large difference in the molecular weights of the reaction partners. The data in Table I illustrate this point. Assuming that the degree of polymerization of the macromer $\overline{DP}_{n1}$ is hundred times larger than that of the small monomer $\overline{DP}_{n2}$, the weight concentration of the latter in the charge becomes almost negligible even at very high molar concentration levels, i.e., $w_2 = 0.038$ at $n_2 = 0.8$. In practice, then, meaningful quantitative composition data could be obtained only over a very narrow concentration range, say, $n_2 > 0.8$ or $n_1 < 0.2$.

Also, at high molar macromer concentrations in the charge the viscosity of the system would become prohibitively large and the reactivity ratios would become diffusion controlled.

Evidently, meaningful copolymer composition data can only be obtained over a narrow low macromer concentration range which severely limits the utility of the least squares methods. Thus calculations may yield correct $r_2$ values, however, would lead to erroneous $r_1$ values.

Milkovich and Chang (9) suggested that by assuming $[M_1] << [M_2]$, $r_2$ can be determined by eq (6) or by the equivalent form:

$$r_2 = \frac{dp_2}{dp_1} \tag{7}$$

where $p_1$ and $p_2$ are partial conversions of macromer and small monomer, respectively. While eq (7) is rigorously valid only at infinitesimally low conversions, in practice it yields satisfactory results at reasonably low (<5%) conversions. It is difficult to obtain accurate results in the copolymerization of macromers with small monomers because it is difficult to stop the copolymerization at very low conversions and even if low conversions could be achieved the quantitative removal of unreacted species (particularly that of the macromer) would be extremely cumbersome and would inevitably lead to unacceptably large experimental error.

These difficulties can be avoided by integrating equation (6) (see for example ref. 10):

$$(\ln[M_1]_o - \ln[M_1]) = \frac{1}{r_2} (\ln[M_2]_o - \ln[M_2]) \tag{8}$$

or

$$r_2 = \frac{\ln(1 - p_2)}{\ln(1 - p_1)} \tag{9}$$

The applicability of eq (9) is illustrated by recent experimental data shown in Table II concerning the free-radical copolymerization of polyisobutenylstyrene ($CH_2$=CH-$C_6H_4$-PIB, PIB-St) macromer with styrene (St). The synthesis of the PIB-St is the subject of a preliminary report (2) and further improved procedures have recently become available (1). The

TABLE I

Mole and Weight Ratio in a Copolymerization System Comprising a Macromer and Small Monomer ($\overline{DP}_{n1} = 100\ \overline{DP}_{n2}$)

| Macromer | | Small Monomer | |
|---|---|---|---|
| mole<br>$n_1$ | wt.<br>$w_1$ | mole<br>$n_2$ | Wt.<br>$w_2$ |
| 0.0 | 0.0 | 1.0 | 1.0 |
| 0.1 | 0.917 | 0.9 | 0.083 |
| 0.2 | 0.962 | 0.8 | 0.038 |
| 0.3 | 0.977 | 0.7 | 0.023 |
| 0.4 | 0.985 | 0.6 | 0.015 |
| 0.5 | 0.990 | 0.5 | 0.010 |
| 0.6 | 0.993 | 0.4 | 0.007 |
| 0.7 | 0.996 | 0.3 | 0.004 |
| 0.8 | 0.998 | 0.2 | 0.002 |
| 0.9 | 0.999 | 0.1 | 0.001 |
| 1.0 | 1.0 | 0.0 | 0.0 |

TABLE II

Copolymerization of Polyisobutenylstyrene Macromer ($M_1$) with Styrene ($M_2$)[a]

| Monomer conc. | | Conversion of | | PIB Content in | | $r_2$ |
|---|---|---|---|---|---|---|
| PIB-St[b] | St | PIB-St | St | Graft Copolymer[c] | | |
| x10$^3$M | M | % | % | mol-% | wt-% | |
| 2.2 | 1.0 | 3.5 | 7.5 | 14.6 | 8.6 | 2.2 |
| 2.6 | 1.0 | 10.9 | 21.6 | 17.9 | 10.7 | 2.1 |
| 3.1 | 1.0 | 11.9 | 23.7 | 20.7 | 12.5 | 2.1 |

[a] In benzene (op ml) with 0.9 mol-% of AIBN as initiator at 60°C

[b] $\overline{M}_n = 9.6 \times 10^3$ by GPC

[c] by $^1$H NMR

$\overline{M}_n$ of the PIB-St macromers were 22,000 - 31,000 and the conversions were relatively high, discouraging the use of differential forms of the copolymerization composition equation. The $r_2$ values calculated by eq (9) are 2.1 ± 0.1.

A final comment concerns the error of $r_2$ estimation. In deriving eq (6) we have introduced two simplifications i.e., $1 >> r_1[M_1]/[M_2]$ and $r_2 >> [M_1]/[M_2]$. Since macromers are hard to homopolymerize (11,12) $r_1$ is negligible, and the source of error is most likely the second assumption. According to the available data the ratio $([M_1]/[M_2])/r_2$ is very small, for example, for the first set of data $2.2 \times 10^{-2}/2.2 = 1.0 \times 10^{-2}$, or 1.0%.

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